1,154,633

Index at acceptance :—Cl AK4

Int. Cl.:—C 01 b 31/06

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COMPLETE SPECIFICATION

Synthetic Diamantiferous Material

We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61, Broadway, New York 6,
5 New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following
10 statement: —

This invention relates to synthetic diamantiferous material.

The present invention provides a synthetic diamantiferous material composed of indi-
15 vidual diamond particles having an average diameter not exceeding 0.1 micron, a surface area between 40 and 400 square metres per gram, and having at least 10% of the surface area containing hydroxyl, carboxyl and car-
20 bonyl functional groups; the said diamond particles being free of defined external crystal faces detectable by optical microscopic examination.

In the accompanying drawings: Figure 1 is
25 a photomicrograph illustrating the crystal structure of the diamentiferous material of the present invention; Figure 2 is a photomicrograph illustrating the crystal structure of natural diamonds; Figure 3 is an infra-red
30 spectrogram of a typical sample of diamantiferous material of this invention when anhydrous; Figure 4 is an infra-red spectrogram of the diamantiferous material of Figure 3 when slightly hydrated; Figure 5 is a Brunauer-
35 Emmet-Teller isotherm of argon adsorption of a typical sample of diamantiferous material of this invention; Figure 6 shows ammonia adsorption isotherms on a typical diamond sample of the present invention; and Figures
40 7 to 12 are photomicrographs illustrating hardness properties of the diamantiferous material of the invention.

The novel diamantiferous material is composed of finely-divided individual diamond
45 particles having a hydrophilic surface exhibiting acidic properties. This synthetic dia-

mond material is produced, in accordance with the invention, by oxidizing "shock loaded graphite", i.e. graphite which has been exposed to shock pressures within the region 50 of diamond stability, with nitric acid at at least 280°C., and preferably at above 300°C. and at atmospheric pressure. The synthetic diamond particles so produced are then recovered and constitute the novel product of 55 the present invention.

The finely-divided diamond particles of this invention have a metallic grey lustre. Calculation of their average surface area and diameter from Brunauer-Emmet-Teller iso- 60 therms measured on representative samples yields a surface area ranging from 40 to 400 square metres per gram, generally 100 to 300 square metres per gram, and an average diameter not exceeding 0.1 microns, generally 65 between 7×10^{-4} and 1×10^{-2} microns. High resolution electron micrographs (one of which is shown in Figure 1) verify that the average particle diameter of the individual diamond particles is within the range specified. 70 In addition, the novel diamond particles have no detectable external crystal faces, even when examined at approximately 100,000 magnification under the electron microscope. Even at these extreme magnifications, microscopic 75 examinations indicate that the diamantiferous material of the present invention is a mass of intertwined diamond crystallites containing so many dislocations that defined crystal faces are not visible. Nevertheless, the existence of 80 sufficiently well-developed diamond crystal lattices has been demonstrated clearly by X-ray diffraction patterns. The absence of defined external crystal faces, which are characteristic of diamonds found in nature and 85 of diamonds produced by other synthetic methods, as described for example, in United States Patent No. 2,947,610 is believed to be unique to the diamantiferous material of the present invention. 90

The surface features of the diamond particles of the present invention may clearly be

noted from Figure 1, which is a photomicrograph of representative diamond particles of the invention. Aggregates comprised of particles not greater than 1×10^{-2} microns in size are visible, corresponding to a particle size of not greater than 100 Å units. The dark structure near the top-left corner of the Figure is believed to be an agglomerate of particles. This Figure also shows the quasi-amorphous rounded surface edges of the diamond particles. The absence of any external well-defined crystal faces is readily evident. In contradistinction, the crystallinity of natural diamonds, having readily discernible sharp-edged fragments, is evident from Figure 2, which is a photomicrograph of a natural diamond marketed as "2-micron diamond powder" by the Geo-Sciences Instrument Corporation. Furthermore, when the crystal face of natural diamond is etched by oxidation, the indentations which are formed appear as inverted pyramidal defects; the defects visible in Figure 1 give no indication of being pyramidal.

In addition to being particularly finely-divided and having no detectable external crystal faces, the diamantiferous material of the present invention has a hydrophilic surface exhibiting acidic properties. Because of the nitric acid oxidation at elevated temperatures, the surface of the diamond crystallites is identifiably altered. The diamantiferous product of the oxidation process has at least 10%, and preferably at least 20%, but generally not more than 30%, of its surface, attached to hydroxyl, carboxyl and carbonyl functional groups, the percentages being based on the total surface area of the diamond particles. In certain instances, depending upon the reaction conditions employed during the oxidation, other oxygen-containing groups such as the products of reaction of these functional groups with each other and the surface atoms of the diamond crystallites, e.g. anhydride, lactone and ether structures, have also been found to be attached to the surface of the diamond crystallites. Infra-red spectrograms of the new diamantiferous material, when anhydrous, indicate characteristic infra-red absorption peaks at the wave lengths 5.65 and 16.2 microns and broad bands of absorption at the wave lengths 2.8 to 3.5 microns and 9.2 to 9.8 microns, and, when hydrated, characteristic infra-red absorption peaks and bands of absorption at the wave lengths indicated when anhydrous, plus an additional infra-red absorption peak at the wave length 6.1 microns and more intense absorption in the region of about 2.9 microns.

Since considerable amounts of oxygen-containing functional groups are attached to the surface of the diamond particles, the carbon content of the new diamantiferous material, as determined by microanalytical methods, is appreciably below the carbon content found in natural diamonds and in man-made diamonds formed by other synthetic methods, which are described as being identical to natural diamonds. Because of the presence of the indicated quantity of oxygen-containing functional groups on the surface of the diamond crystallites, the new diamantiferous material has a carbon content between 80 and 95%, preferably between 87 and 92% by weight, a hydrogen content between 0.2 and 2%, preferably between 0.5 and 1.5% by weight, a nitrogen content between 0.1 and 2.5% by weight, and an ash content not exceeding 1.0% by weight after being dried in air at a temperature of 200°C. for a period of at least 2 hours for removal of water and other volatile foreign adsorbed materials.

It has been also found that the new diamantiferous material, unlike most natural diamonds or man-made diamonds manufactured by other synthetic methods, blackens when heated in an argon atmosphere at a temperature in the range from 850° to 900°C. for a period of 4 hours. As a result of this heating, the diamantiferous material of this invention can normally be recognised by the loss of at least 5%, generally at least 8%, of its weight in the form of carbon monoxide, carbon dioxide, water and hydrogen. The darkening effect is ascribed to the removal of relatively gross quantities of surface oxygen-containing functional groups, as a result of which the colour of the underlying diamond matrix is exposed. Examination of the blackened material by X-ray crystallographic method indicates the presence of diffraction patterns characteristic of diamond.

In our specification No. 1,077,469 we describe a method of producing diamond from another form of carbon, which comprises subjecting a body of said carbon to an explosively generated shock wave which impinges on substantially the whole of at least one face of the said body of carbon and whose amplitude is so correlated with the density of said carbon that it develops therein a maximum temperature below 2000°C. and a pressure from 100 to 700 kilobars sufficient to convert at least part of the said carbon into diamond. The product of the process of our Specification No. 1,077,469, when the body of carbon is graphite, is "shock-loaded graphite", containing synthetic diamond, and is a particularly useful starting material for the nitric acid oxidation process by which the diamantiferous material of the present invention is produced. Reference is made to this earlier application for a detailed description of the process.

In general, the crude product resulting from the shock treatment contains less than 15% diamond, based on the carbon content, and is usually contaminated with gross amounts of inorganic materials. Microscopic examination reveals that the diamond particles are embedded within pockets of unreacted graphite and other contaminants and that the particle

size of the shoc[●]ed graphite varies in general from 30[●]1000 microns. After removal of inorganic impurities by chemical treatment, the "shock-loaded graphite", contaminated with unconverted graphite, as determined by microanalytical methods, ordinarily contains at least 99.0% carbon and not more than 1.0% hydrogen. Within the particles of shock-loaded graphite are the small synthetic diamonds which are oxidised in accordance with the present invention.

As previously indicated, the diamantiferous product of the present invention is obtained by nitric acid oxidation of "shock-loaded graphite". The "shock-loaded graphite" starting material is normally contaminated with substantial quantities of unconverted graphite and inorganic impurities containing silicon, iron, boron, aluminium, calcium and titanium. Preferably, removal of the major portion of the inorganic impurities is effected by conventional methods, e.g. by treatment with a mineral non-oxidising acid such as hydrochloric acid and/or an inorganic base such as potassium hydroxide, prior to subjection of the "shock loaded graphite" starting material to the oxidation process. To produce a diamantiferous product having the unique crystalline shape, particle size and surface structure above-described, it has been found that, at atmospheric pressure, temperatures of at least 280°C., and preferably above 300°C., must be employed. The reaction time, in general, is dependent upon the solids content of the starting material present in the oxidation zone during the reaction and may vary e.g. from 2 to 60 hours, and is preferably from 10 to 40 hours for feeds containing 1 to 30% solids, based on the total weight of the contents of the oxidation zone. Nitric acid concentrations above 50% are generally suitable, although at the elevated temperature required, nitric acid concentrations above 65% are preferred. When operating at atmospheric pressures, the stated elevated temperature may normally be maintained for the required period by employing, as a reaction medium, one or more concentrated mineral acids such as sulphuric or phosphoric acid, salts of mineral acids, especially alkali metal sulphates such as potassium sulphate, or mixtures thereof. If desired, superatmospheric pressures up to 250 atmospheres may be used with correspondingly shorter reaction time. After completion of the oxidation, the diamantiferous material is recovered by conventional means, as by decantation, and residual acid is washed therefrom with water. Although this product may be used without further purification in chromatographic and bearing applications, it is preferred to remove residual inorganic impurities by methods similar to those employed prior to oxidation, as described above, before the material is used for its intended purpose. The diamantiferous material resulting from the before-described process exhibits the characteristic X-ray diffraction pattern for diamond; is substantially free of graphite, generally containing quantities less than that detectable (0.2%) by powder X-ray diffraction methods; and contains less than 0.2% of inorganic contaminates, as determined by emission spectroscopy. In addition, X-ray spectra of the synthetic diamantiferous material of the present invention do not reveal the presence of alumina, silicon carbide or boron carbide.

The following Example illustrates the preparation of the new diamantiferous material.

EXAMPLE

A sample of "shock loaded graphite" containing substantial quantities of unreacted graphite and inorganic contaminants was screened through a 60-mesh United States Standard screen. 1200 grams of screened material were treated with 1.5 kilograms of 35% HCl at the boiling temperature of the mixture to remove lime and other inorganic impurities. After digestion for 3 hours, 492 grams of a solid residue were obtained. To this residue 450 grams of 60% hydrogen fluoride were added and the resulting mixture was heated to its boiling temperature until all of the hydrogen fluoride added had evaporated. The resulting residue was mixed with 600 grams of potassium hydroxide pellets, and the resulting mass was treated with water to dissolve any soluble constituents present in the mixture. The liquid phase of the mixture was decanted, and the residual solids were first washed with water and finally with 30% HCl to remove residual potassium hydroxide. The recovered solid was then dried at 400°F. for 2 hours. Microanalytical and emission spectrographic analysis of the dried solid indicated a carbon content of 99.2%, a hydrogen content of 0.5%, a silicon content of 0.01%, a calcium content of 0.01% and the presence of trace amounts of magnesium, copper and titanium. The dried solid exhibited an X-ray diffraction pattern characteristic of diamond, and comparison of this pattern with standardized X-ray patterns containing known amounts of diamond showed that the dried solid residue contained about 12% diamond, the remainder being substantially graphite.

20 grams of the dried solid residue were then added to 500 millilitres of a 10:1 concentrated $H_2SO_4:H_3PO_4$ acid mixture. The resulting mixture was heated to 320°C. at which temperature 1.5 kilograms of 70% nitric acid were added dropwise to the mixture over a period of $2\frac{1}{2}$ hours. After completion of the digestion, the mixture was cooled to room temperature, liquid acid was decanted from the solid, and the resulting slurry was washed with water and dried. The dry residue was mixed with 10 grams of potassium hydroxide pellets and then treated with water

to dissolve any soluble constituents present therein. The liquid phase was decanted and the residual solids were washed with water and then with 30% HCl to ensure removal of residual potassium hydroxide. After the residue had been dried at 200°C. for a period of 2 hours, 2.2 grams of the desired synthetic diamond product were obtained. X-ray diffraction patterns of the product indicated the presence of diamond with no detectable amount of graphite (less than 0.2%). Microanalytical examination of the product showed a carbon content of 87.8%, a hydrogen content of 1.1% and a nitrogen content of 1.94%. Emission spectroscopic examination indicated that less than 0.2% of inorganic impurities were present. The oxygen content, determined by difference, was about 10.0%.

The infra-red spectrum of the oxidized diamond product, shown in Figure 3, was measured by the standard potassium bromide pellet method, after heating the sample to 300°C. for a period of 2 hours to remove any adsorbed water. As is evident therefrom, the anhydrous diamond has characteristic absorption peaks at the wave lengths 5.65 and 16.2 microns and broad bands of absorption at the wave lengths 2.8 to 3.5 and 9.2 to 9.8 microns. The hygroscopic properties of the oxidized diamond were observed from Figure 4, which is the infra-red spectrum of the identical salt plate used in obtaining the spectrogram illustrated in Figure 3, after being permitted to stand at about 25°C. and 70% relative humidity for a period of about 10 hours. As is readily observed therefrom, an additional absorption peak at the wave length 6.1 microns and more intense absorption in the region of about 2.9 microns, believed to be attributable to adsorbed water, now appear in the spectrogram of the slightly hydrated diamond. In obtaining the spectrograms shown in Figures 3 and 4, pellet mixtures of diamond and potassium bromide, having a ratio of 0.0327 grams of diamond per gram of potassium bromide were employed.

The surface area of the oxidized diamond particles, obtained as in the Example above, was determined to be 220 square metres per gram as calculated from a Brunauer-Emmet-Teller isotherm representing argon adsorption on the diamond sample at 78°K., as illustrated in Figure 5. A plot of the left side of the Brunauer-Emmet-Teller equation, normally written in the form:

$$\frac{x}{V(1-x)} = \frac{1}{V_m C} + \frac{(C-1)x}{V_m C}$$

(wherein x is a relative pressure $\frac{P}{P_0}$, and P is the pressure at each isotherm point and P_0 is the measured vapour pressure of bulk argon

at the isotherm temperature; V is the volume of argon gas adsorbed on the diamond surface; C is a constant, determined in the instant example to be 85.2; and V_m is the volume of argon gas needed to form a unimolecular layer on the surface of the test material) against x affords a means of ascertaining whether or not the adsorption data obeys such an equation and also of evaluating V_m, the volume of gas needed to form a monolayer on the test material surface. From the plot illustrated in Figure 5, wherein Y is the function $\frac{x}{V(1-x)}$ and y is measured in n', V_m was determined to be 58.7 cubic centimetres per gram. Using an atomic area of 14 $Å^2$ for the argon atom, the specific surface becomes 220 square metres per gram.

The average diameter of the individual diamond particles, obtained as in the Example, was determined to be 85 Å per particle. This result was calculated from the equation:

$$\frac{A}{V} = \frac{(N)4r^2}{(N)4/3r^3}$$

wherein A, the surface area of the sample is 220 square metres per gram; V, the volume of 1 gram of diamond sample, is the reciprocal of the diamond density (3.51 grams per cubic centimetre), N is the total number of particles contained in one gram of diamond sample and r is the diamond particle radius.

The nature and the quantity of the oxygen-containing functional groups chemisorbed or chemically combined on the diamond surface of the diamond particles was determined by reaction of a sample of diamond, obtained as in the Example, with potassium metal and from gas adsorption data of ammonia at 0°C.

To determine the quantity of hydroxyl, carboxyl and carbonyl groups present on the surface, 1 gram of diamond was reacted with potassium metal by distilling an excess of potassium into a sample of the diamond over a high vacuum. After heating the sample for one hour at 250°C., the excess potassium was distilled off the diamond at a temperature below 400°C. Distillation of the potassium was considered to be complete when a metallic mirror no longer formed above the diamond particles. At the conclusion of the run, after the diamond samples had been sealed off from the vacuum apparatus, a portion of the potassium-treated diamond was weighed, suspended in distilled water and the resulting solution was titrated with aqueous 0.1N HCl. The results showed that 1.58 millimoles of potassium reacted with the surface of 1 gram of diamond which indicates that about 22% of the diamond surface was covered with hydroxyl, carboxyl and carbonyl functional groups.

To determine fraction of the surface covered with carboxyl groups, ammonia isotherms, illustrated in Figure 6, were measured on samples of the oxidized diamond, obtained
5 as in the Example, which had been outgassed overnight at 240°C. at pressures below 10⁻¹ mm. Hg. As may be seen therefrom, the ammonia isotherms closely follow the "volume adsorbed" axis at low pressures,
10 which is characteristic of both strong physical adsorption and chemisorption. To measure the amount of chemisorption, the isotherm labelled A was first measured at 0°C. on outgassed diamond. Sample diamond was then outgassed
15 overnight at room temperature to remove only the physically adsorbed ammonia and the ammonia isotherms labelled B was then measured at 0°C. The difference in volume adsorbed between the parallel curves A and B
20 at equal pressure are considered to be the amount of chemisorbed ammonia present on the surface as NH_4^+ groups. By this procedure, the amount of chemisorbed ammonia was determined to be 0.14 millimoles per
25 gram of diamond sample, which indicates that about 2% of the diamond surface was covered with carboxyl functional groups. A third ammonia isotherm, measured at 0°C., after the diamond had been outgassed overnight at
30 240°C., is shown by the circular points which lie identically on top of curve A. This isotherm demonstrates that the acidic surface sites were not destroyed by heating to temperatures of about 240°C.
35 The hardness of the diamantiferous material of the present invention was determined by abrading polished synthetic sapphire, polished tungsten carbide and polished natural diamond faces with the product obtained from the
40 Example. Since the hardness of these materials is nine or higher on the Mohs scale and X-ray diffraction patterns of the diamond material did not reveal the presence of any hard material, such as alumina, silicon carbide
45 or boron carbide, it is concluded that the synthetic diamantiferous material of the invention also possesses a hardness of ten on the Mohs scale.
Visual evidence of the hardness of the new
50 diamantiferous material may be observed from Figures 7 to 12, which are photomicrographs of polished surfaces of substances having Mohs hardnesses of nine or ten before and after abrasion with the diamantiferous material of
55 the present invention.
Figures 7 and 8 are photomicrographs at magnifications of 33 times of the surface of a synthetic sapphire plate. The features visible in Figure 7 are scratches made with a diamond-pointed tool; these scratches were used for
60 locating the same area in subsequent microscopic examinations. The abraded surface of the sapphire plate is plainly visible from Figure 8 after a small amount of our synthetic diamantiferous material was placed on the
65 plate and rubbed into its surface.
Figures 9 and 10 are photomicrographs at magnifications of 400 times of a polished natural diamond face. The characteristic cleavage line of the natural diamond through
70 the centre of Figure 9 may be readily noted. The abraded surface of the natural diamond after our synthetic diamantiferous material had been placed on the natural diamond face and pressure applied thereto by the fingers via an
75 intermediate glass plate is shown in Figure 10. This proves that the diamantiferous material of the present invention possesses a Mohs hardness of ten.
Figures 11 and 12 are photomicrographs at
80 magnifications of 400 times of a polished tungsten carbide face. The two indentations visible in Figure 11 are fiducial points made with a diamond tool under pressure. The abraded surface of the tungsten carbide face
85 after rubbing with a sample of the new synthetic diamantiferous material is readily apparent from Figure 12.
As indicated above, the synthetic diamantiferous material of the present invention exhibits
90 improved load bearing and chromatograph properties.
To evaluate the load bearing properties of the new synthetic diamond material Falex tests were carried out using the diamond obtained
95 as in the Example. In this test, metal an metal-diamond coated cylindrical pins were rotated between two steel lever arms by applying a compressive load on the test pin. This load and the resulting torque are measured by
100 suitable gauge mounted on the instrument. The test was carried out in heavy mineral oil, having a Saybolt viscosity of 360 and 390 units at 100°F.; the oil is used to dissipate the heat evolved during rotation of the test pin.
105 Time, temperature, load and torque are recorded during the test and, at regular intervals, the load on the rotating test Falex pin is increased. A short "run-in" period of minimal loading usually precedes the heavier
110 loads. The test was continued until failure of the coated Falex pin occurred. The results of the test are recorded in Table I below.

TABLE I

Test Surface Applied to Falex Pin	Plating Conditions Used to Apply Test Surface to Falex Pin				Wear Qualities and Lubricity at Failure		
	Current (Amps.)	Time (Min.)	Temperature (°F.)	Weight of Plate (grams)	Load (lbs.)	Torque (in. lbs.)	Coefficient of Friction
Chromium-Diamond	10	30	130	0.1184	2600	62	0.071 (a)
Bronze-Diamond	0.1	80	70	0.0680	1700	42	0.0735 (b)
Chromium	10	30	130	0.1422	1600	64	0.1188 (a)
Bronze	0.1	80	70	0.1424	550	25	0.135 (b)

(a) Break-in time was 5 minutes with no recorded load on the test pin. The test was then run for 5 minutes with 250 pounds of load on the test pin; thereafter, the load was raised by 50 pounds at the end of every minute until the end of the test.

(b) Break-in time was 5 minutes with no recorded load on the test pin. The test was then run for 5 minutes with 250 pounds of load on the test pin; thereafter, the load was raised 50 pounds every 5 minutes up to 55 minutes. The time interval was then changed to 2 minutes for the next 50 pound load increment, 3 minutes for the next increment and 2 minutes, thereafter up to 66 minutes. After this time, the load was raised 50 pounds every minute until the end of the test.

In each of the above tests, the diamond-metal coating proved capable of carrying a greater bearing load than the metal coating alone. In addition, the diamond-metal coating exhibited a lower coefficient of friction at the higher bearing loads than the metal coating alone. The combination of these two properties is desirable for any bearing surface where sliding friction is encountered and indicates that the diamond-metal composite is superior to diamond-free metal bearing surfaces.

To demonstrate the chromatographic properties of the new synthetic diamond material, a mixture of air, carbon tetrafluoride, tetrafluoroethylene, 1,1-difluoroethylene and difluoromethane was injected into an F & M Model 500 Gas Chromatograph equipped with an eight foot length copper column (1/4" outer diameter) filled with the diamond obtained as in the Example. The mixture was separated into its individual components after a period of about 20 minutes, using helium as a carrier gas, the temperature of the column and the current of the detector block being maintained at 68°F. and 150 milliamps respectively. The observed relative retention times are listed in Table II below.

TABLE II

Component	Relative Retention Time
Air	0.00
CF_4	0.09
$CF_2=CF_2$	0.38
$CH_2=CF_2$	0.61
CH_2F_2	1.34

It is evident from these results that the new synthetic diamantiferous material exhibits useful chromatographic properties.

WHAT WE CLAIM IS:—

1. A synthetic diamantiferous material composed of individual diamond particles having an average diameter not exceeding 0.1 micron, a surface area between 40 and 400 square meter per gram, and having at least 10% of the surface area containing hydroxyl, carboxyl and carbonyl functional groups, the said diamond particles being free of defined external crystal forms detectable by optical microscopic examination.

2. A diamantiferous material according to claim 1, in which the individual diamond particles have an average diameter between 7×10^{-1} and 1×10^{-2} microns, a surface area between 100 and 300 square metres per gram, and at least 20% of the surface area contain hydroxyl, carboxyl and carbonyl functional groups.

3. A diamantiferous material according to claim 1 or 2 having a carbon content between 87% and 92% by weight.

4. A diamantiferous material according to claim 1, 2 or 3 exhibiting, when heated in an argon atmosphere at a temperature in the range from 850°C. to 900°C. for a period of 4 hours, a loss of at least 5% of its weight in the form of carbon monoxide, carbon dioxide, water and hydrogen.

5. A diamantiferous material according to claim 1 substantially as described.

6. Process for the production of a diamantiferous material according to claim 1 which comprises oxidizing " shock-loaded graphite " with nitric acid at at least 280°C.

7. Process according to claim 6 in which the oxidation is effected at above 300°C. and at atmospheric pressure.

8. Process according to claim 6 or 7 in which the " shock-loaded graphite " is subjected, prior to oxidation, to the action of a mineral, non-oxidizing acid, or an inorganic base or both to remove inorganic impurities.

9. Process according to claim 6, 7 or 8 in which the nitric acid is used in a concentration of above 50%.

10. Process according to claim 9 in which the nitric acid is diluted with sulphuric acid, phosphoric acid, an alkali metal sulphate or mixture thereof.

11. Process according to claim 6 substantially as described in the Example.

12. Synthetic diamantiferous material as claimed in claim 1 when produced by the process of any of claims 6 to 11.

J. A. KEMP & CO.,
Chartered Patent Agents,
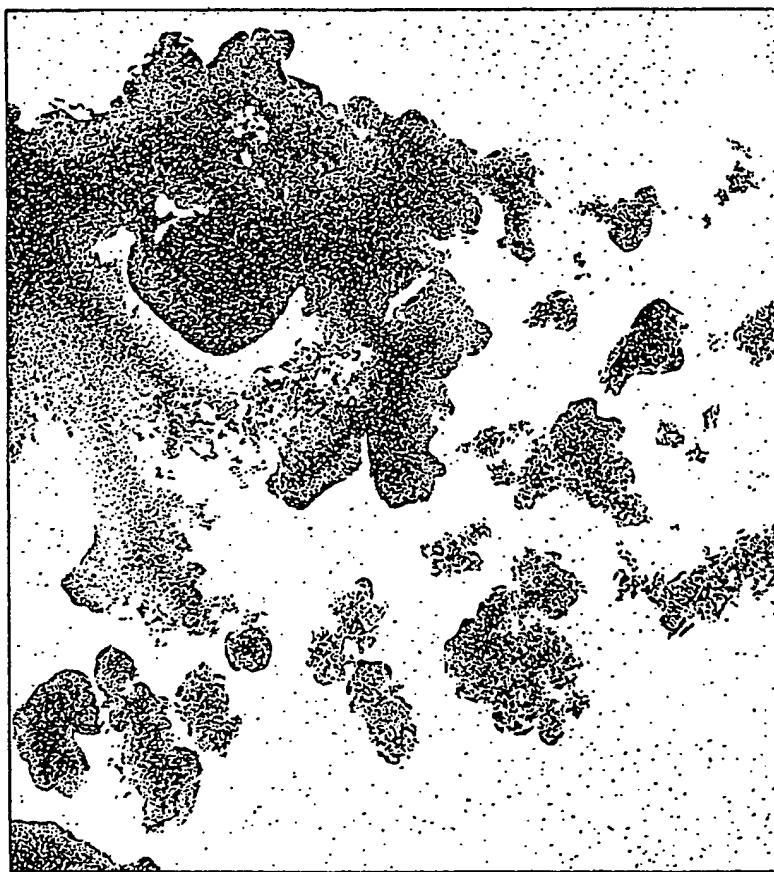14, South Square, Gray's Inn,
London, W.C.1.

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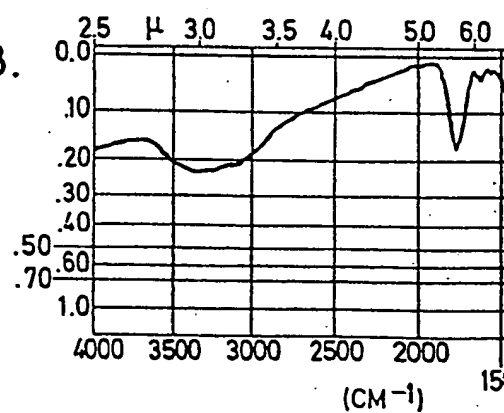the Original on a reduced scale*
Sheet 1

FIG. 1.

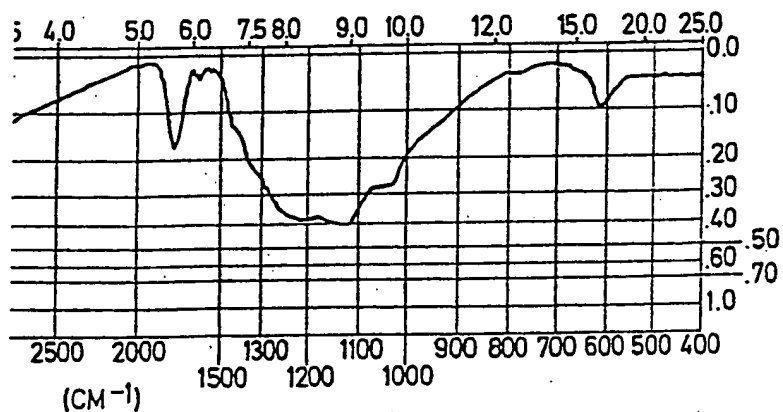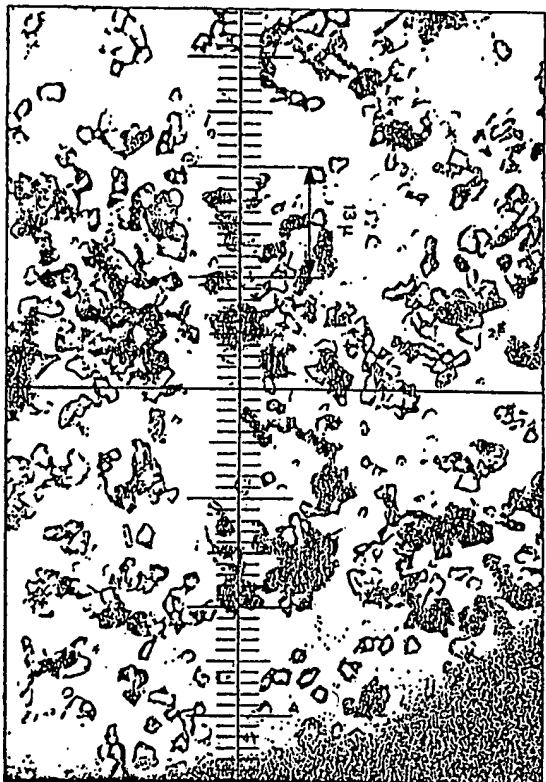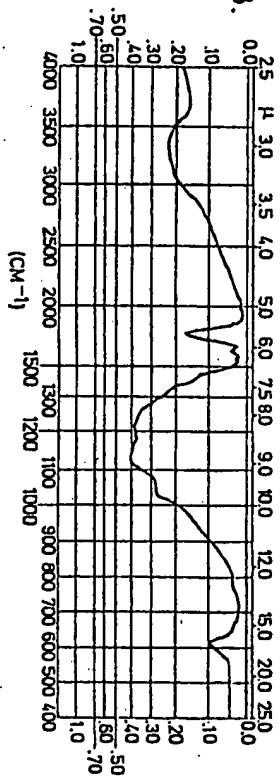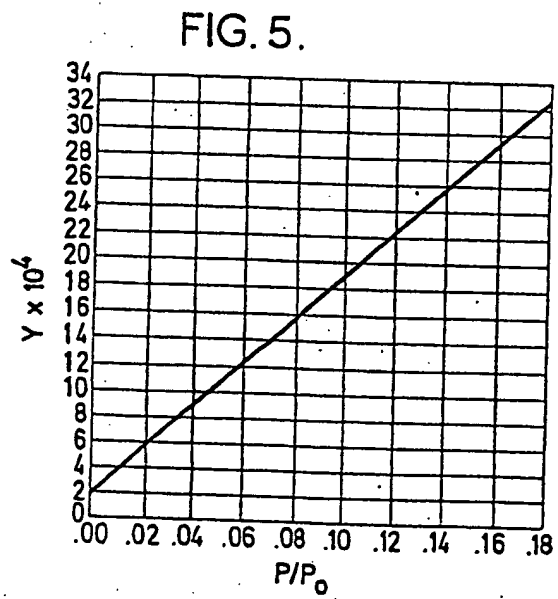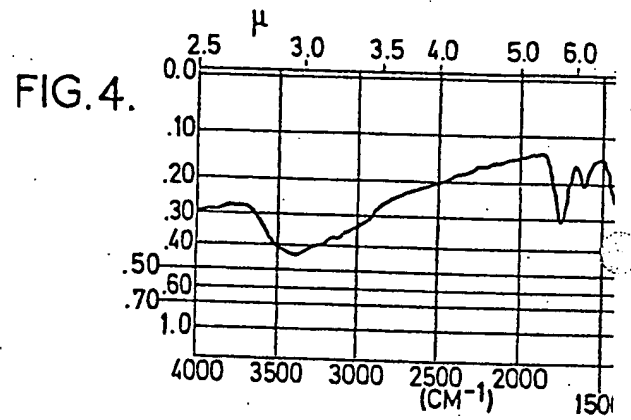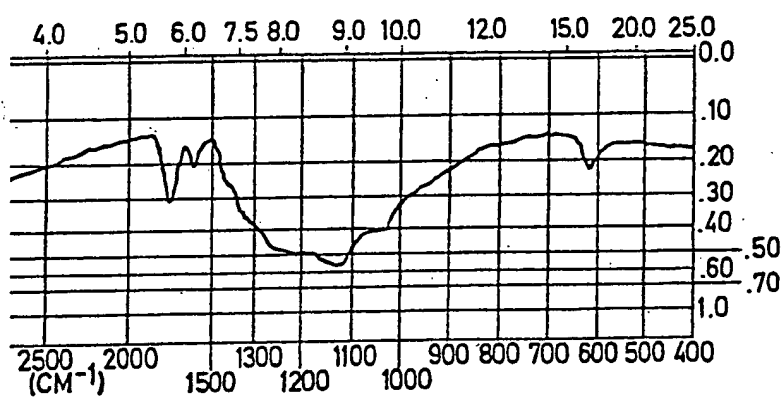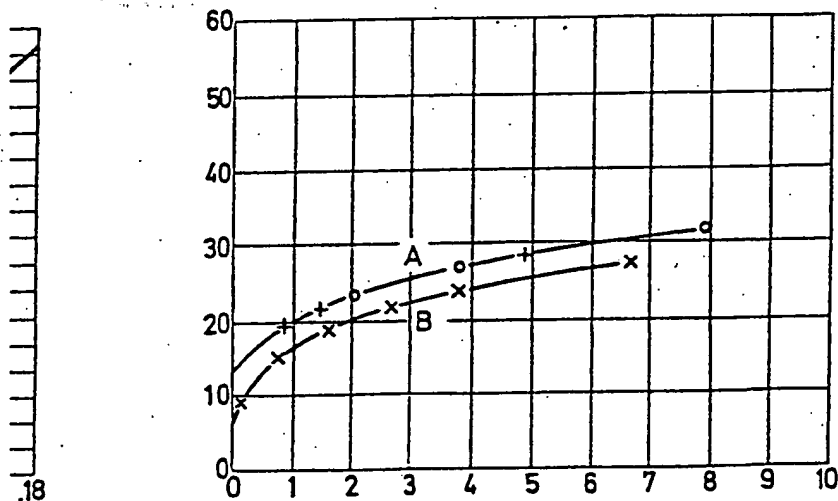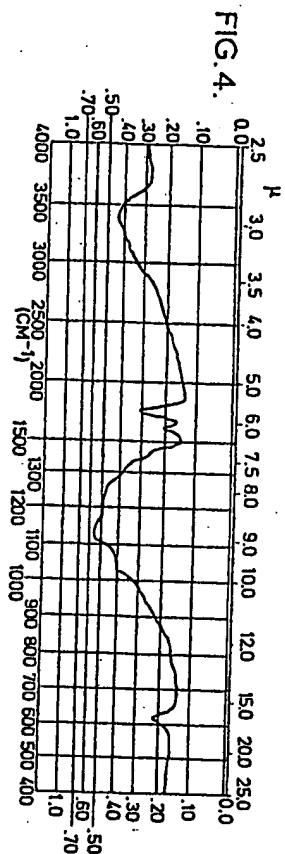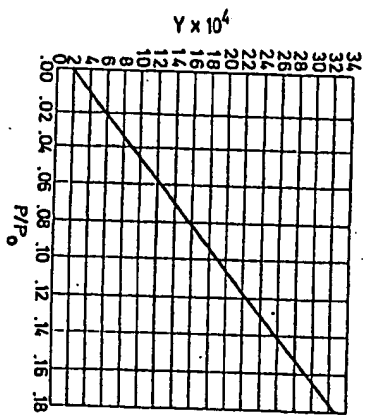O 0·1 0·2 0·3 0·4   microns

FIG. 2.

13 μ

FIG. 3.

2.5   μ 3.0   3.5 4.0   5.0 6.0
0.0
.10
.20
.30
.40
.50
.70 .60
1.0
4000 3500 3000 2500 2000   15

(CM⁻¹)

FIG.2.

FIG.3.

(CM⁻¹)

FIG.4.

μ

2.5　　3.0　　3.5　4.0　　5.0　6.0

0.0
.10
.20
.30
.40
.50
.60
.70
1.0

4000　3500　3000　2500　2000　　1500

(CM⁻¹)

FIG. 5.

Y × 10⁴

34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0

.00 .02 .04 .06 .08 .10 .12 .14 .16 .18

P/P₀

60
50
40
30
20
10
0

FIG. 6.

FIG. 4.

FIG. 5.

FIG. 6.